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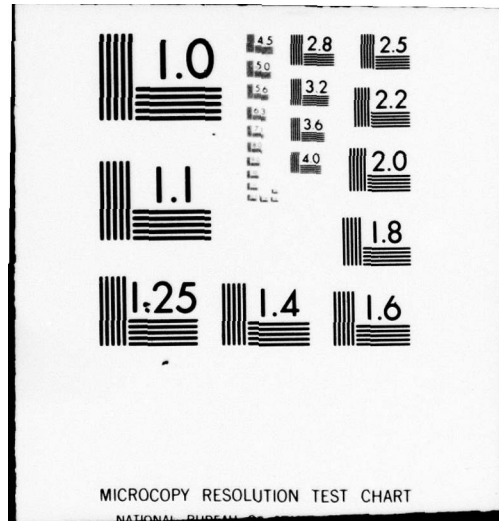
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DEPTH AND CARRIER CONCENTRATION OF PHOTOLUMINESCENCE

FEATURES IN HEAT TREATED GaAs:Si

Technical Report: May 1979

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by

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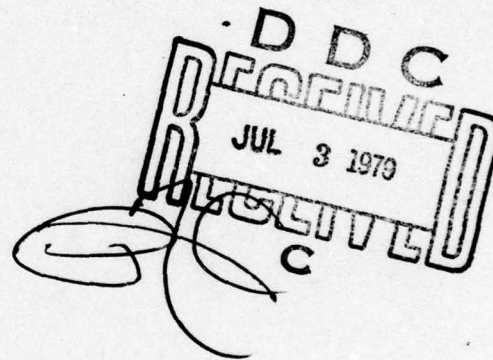
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Report SF21

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DEPTH AND CARRIER CONCENTRATION DEPENDENCE OF PHOTOLUMINESCENCE
FEATURES IN HEAT TREATED GaAs:Si

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ABSTRACT

The photoluminescence (PL) spectra of silicon doped n-type GaAs of four different carrier concentrations from 4×10^{15} to $3 \times 10^{18} \text{ cm}^{-3}$ were examined. Successive measurements as the samples were annealed for times from 15 to 60 minutes at 600-700°C, and as they were successively etched back, revealed that all PL changes were surface related, with a typical depth of 1 μm .

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I. INTRODUCTION

The photoluminescence (PL) spectrum of gallium arsenide has proven to be a useful tool in the characterization of the electronic levels.⁽¹⁻¹⁰⁾ The spectral features seen can be cataloged in three general categories. First, there are sharp lines at energies just below the band gap, usually attributed to transitions involving the bands, excitons, and/or shallow hydrogenic impurities. Second, there are broader features at energies 0.1 to 0.3 eV less than the band gap which seem to result from complexes involving a gallium or an arsenic vacancy and a nearby substitutional impurity. The interpretation of several of these features, however, has been the subject of considerable controversy. Finally, there are transitions involving the deeper levels which are utilized in compensated, high resistivity substrate material.

The purpose of the work reported here is to examine the dependence of the PL spectrum of silicon doped GaAs on both the electron carrier density and the depth of radiative transitions below the surface. The latter affects are determined by a combination of thermal annealing and controlled chemical etching.

II. EXPERIMENTAL

The silicon doped n-type gallium arsenide samples used were taken from ignots grown in silica crucibles, reducing the likelihood of impurities other than silicon. Polished wafers with $\langle 100 \rangle$ orientation were cut into 1 cm square pieces. Four carrier concentrations were used: 4×10^{15} , 5×10^{16} , 8×10^{17} and $3 \times 10^{18} \text{ cm}^{-3}$. The apparatus for the photoluminescence measurements has been described previously.⁽⁹⁾ Briefly a He-Ne

laser is used for excitation, the dewar can hold four samples at temperatures between 12 and 300 K, and detection is done by a 1/2 meter spectrometer with a silicon p-i-n detector.

Annealing of the GaAs samples was done in a quartz furnace with flowing hydrogen gas. Depth profiling was achieved with one of two types of chemical etchants, depending on the thickness of GaAs to be removed. For 1.5 μ or less, a solution of 5:2:100, $H_2SO_4:H_2O_2:H_2O$ was used; the thickness removed was determined by scanning electron microscopy. For greater depth, a 1:3 bromine:methanol mixture was used and the sample thinned by standard polishing techniques. In this case the amount of material removed was measured by weight loss of the sample.

III. RESULTS

The photoluminescence spectra from the GaAs:Si samples prior to any heat treatment are shown in Fig. 1 for each of the four carrier concentrations studied. Three major features are seen, and we refer to them as Bands I, II and III. There is an orderly development of these features as the carrier concentration is increased. Band I at 1.503 eV at 90 K has been attributed to a transition from a silicon donor (Si_{Ga}) to the valence band. It becomes progressively stronger as the carrier density is increased (see Fig. 2a), increasing by about a factor of 40 over our range of study. We assume that the slightly lower energy (5 meV) observed at $8 \times 10^{17} \text{ cm}^{-3}$ is due to a slightly higher temperature or a difficulty in resolving the doublet structure, and not to a different origin of the transition.

The second peak, Band II at 1.475 eV, is only seen in the more heavily doped samples (see Figs. 1, 2a) and in fact becomes the dominant feature. It is attributed to a donor-acceptor transition between silicon on a

gallium site and silicon on an arsenic site ($\text{Si}_{\text{Ga}} - \text{Si}_{\text{As}}$). This peak, therefore, requires a certain amount of self compensation. Here again at $8 \times 10^{17} \text{ cm}^{-3}$, the peak is ~ 5 meV lower in energy.

The third major feature, Band III at 1.22 eV, has been identified by several authors^(8,10) as a gallium vacancy-donor impurity complex ($\text{Si}_{\text{Ga}} - \text{V}_{\text{Ga}}$ in this case). It also is not seen in the lightly doped material, presumably because the gallium vacancy density is low. In addition to the major peaks, there are weak lines present in the PL spectra whose interpretation is more speculative. Among these are features at 1.485 and 1.40 eV which may be due to carbon impurities, and at 1.45 eV, possibly the result of a silicon-silicon nearest neighbor complex.

After subjecting the GaAs:Si to a moderate temperature anneal, the emission intensities of the PL peaks are altered as shown in Fig. 2b for a 60 min 600°C anneal cycle. For the lightly doped samples, the 1.503 eV peak grows in intensity, while for the heavily doped ones, it remains nearly constant or falls off slightly. Band II, at 1.475 eV also increases in intensity for the lightly doped samples, roughly parallel to Band I, while Band III increases for all carrier concentrations and shifts to slightly higher energies. The time evolution for these processes is shown for one sample ($5 \times 10^{16} \text{ cm}^{-3}$) in Fig. 3 and for the lightest and heaviest doped samples in Ref. 1.

Most noticeable in Fig. 3 is the onset of a new peak at 1.35 to 1.36 eV which we label Band IV. Associated with the major peak is a smaller companion peak due to a LO phonon replica. Band IV is attributed to an arsenic vacancy-silicon acceptor complex ($\text{V}_{\text{As}} - \text{Si}_{\text{As}}$) resulting from the loss of arsenic from the sample surface,⁽¹¹⁾ although other authors have suggested that it is Cu related.^(4,7) It occurs for all carrier concentrations and

all annealing temperatures equal or above 600°C. Except for the most heavily doped material (See Fig. 2b), its intensity seems independent of doping density. It appears, however, (Fig. 3) to drop somewhat in intensity as the annealing time is extended.

The latter point is also illustrated in Fig. 4 for the more lightly doped material. On the same plot, the result of a 6000 Å etch is shown, revealing that the emission in Band IV is substantially reduced. In fact, after this much GaAs is removed, the PL intensity from Band IV seems independent of annealing time. Further etching causes Band IV to disappear completely, confirming that it is due to a surface phenomena. The same information for Band I is also depicted in Fig. 4, showing both the substantial growth of this peak with annealing time, and the reduction in intensity back toward the original value as the surface is etched away.

Another way of examining the effects of annealing is illustrated in the depth profiles of Fig. 5. In this case, the heavily doped GaAs:Si was annealed at a somewhat higher temperature (700°C) for 15 minutes. After removal of about 4 μm the original as-grown spectrum is restored. Bands I and II, which are significantly decreased when annealing at the higher temperature. As the etch back proceeds they return to their original values with a nearly exponential depth dependence. In this case, the depth constant is very close to 1 μm. In contrast, Bands III and IV actually increase in intensity in the first stages of the depth profile. They then fall to their original values, again displaying an exponential constant of approximately 1 μm. Thus all changes in the photoluminescence spectrum are seen to originate in a region very close to the surface of the sample.

IV. DISCUSSION

The two most noticeable changes in the GaAs:Si PL spectrum with heat treatment are the growth of the 1.503 eV line for small original carrier concentrations and the appearance of the 1.36 eV line for all carrier concentrations. Both these changes, as well as the other modifications with annealing, are surface related with a typical depth of 1 μm independent of carrier concentration. They likely result from the escape of arsenic from the surface and the subsequent in-diffusion of arsenic vacancies. The apparent increase in Bands III and IV below the surface of the annealed material (Fig. 5) may be an artifact due to the formation of a surface layer which absorbs more of the lower energy radiation. Such an explanation could also explain the apparent decrease in the 1.36 eV radiation (Fig. 3, 4) as the annealing is continued.

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FIGURE CAPTIONS

- Figure 1: Photoluminescence spectra at 90 K of as-grown GaAs:Si for the four carrier concentrations studied.
- Figure 2: Carrier density dependence of the 90 K emission intensity of the major PL peaks in the material (a) as-grown (b) after 600°C anneal for 60 minutes.
- Figure 3: Time evolution of the 90 K PL spectrum from the $5 \times 10^{16} \text{ cm}^{-3}$ sample after successive 600°C anneals.
- Figure 4: 90 K PL emission intensity of $5 \times 10^{15} \text{ cm}^{-3}$ sample as a function of annealing time at 600°C. Open circles are before etch back; closed circles after 6000Å etch. Band I: 1.503 eV; Band IV: 1.36 eV.
- Figure 5: PL intensities of $3 \times 10^{18} \text{ cm}^{-3}$ samples at 90 K as a function of material etched away following 15 minute anneal at 700°C.

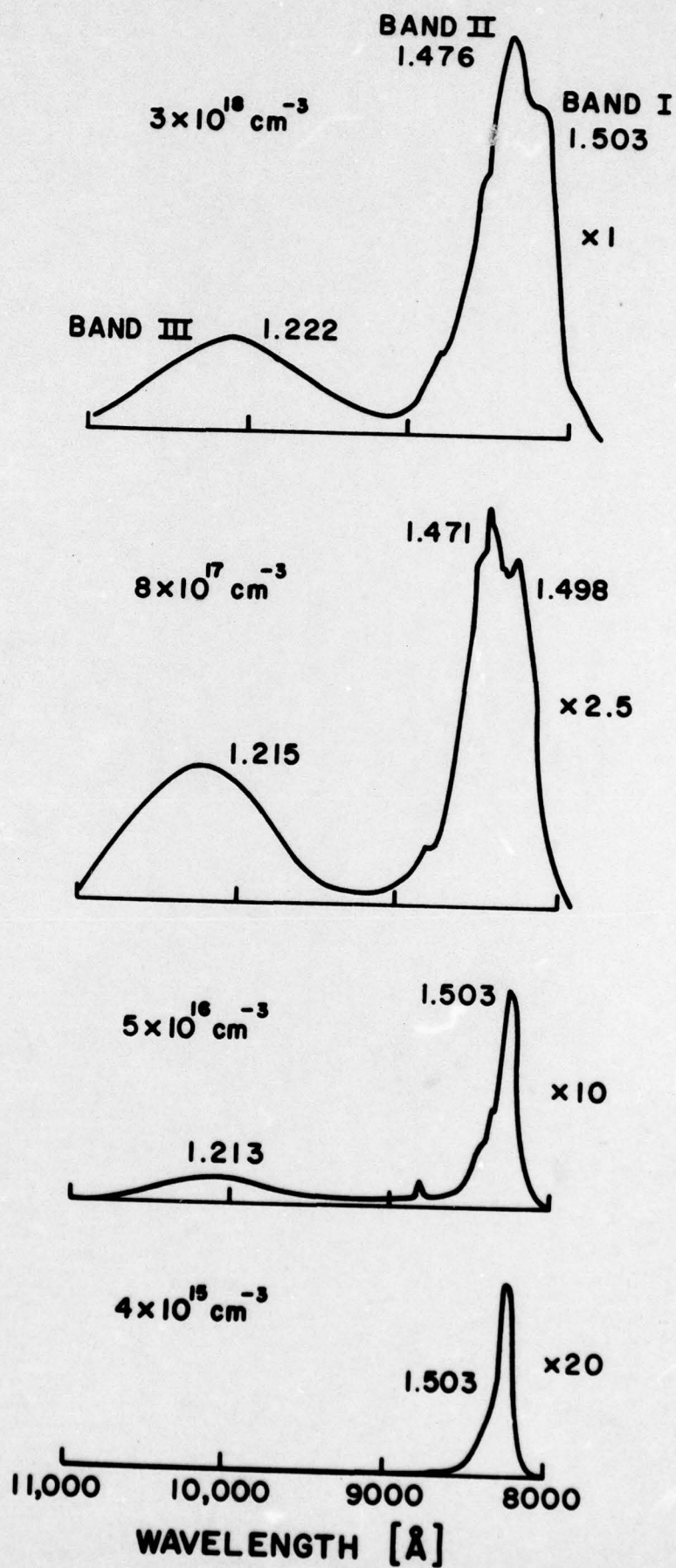


Fig. 1

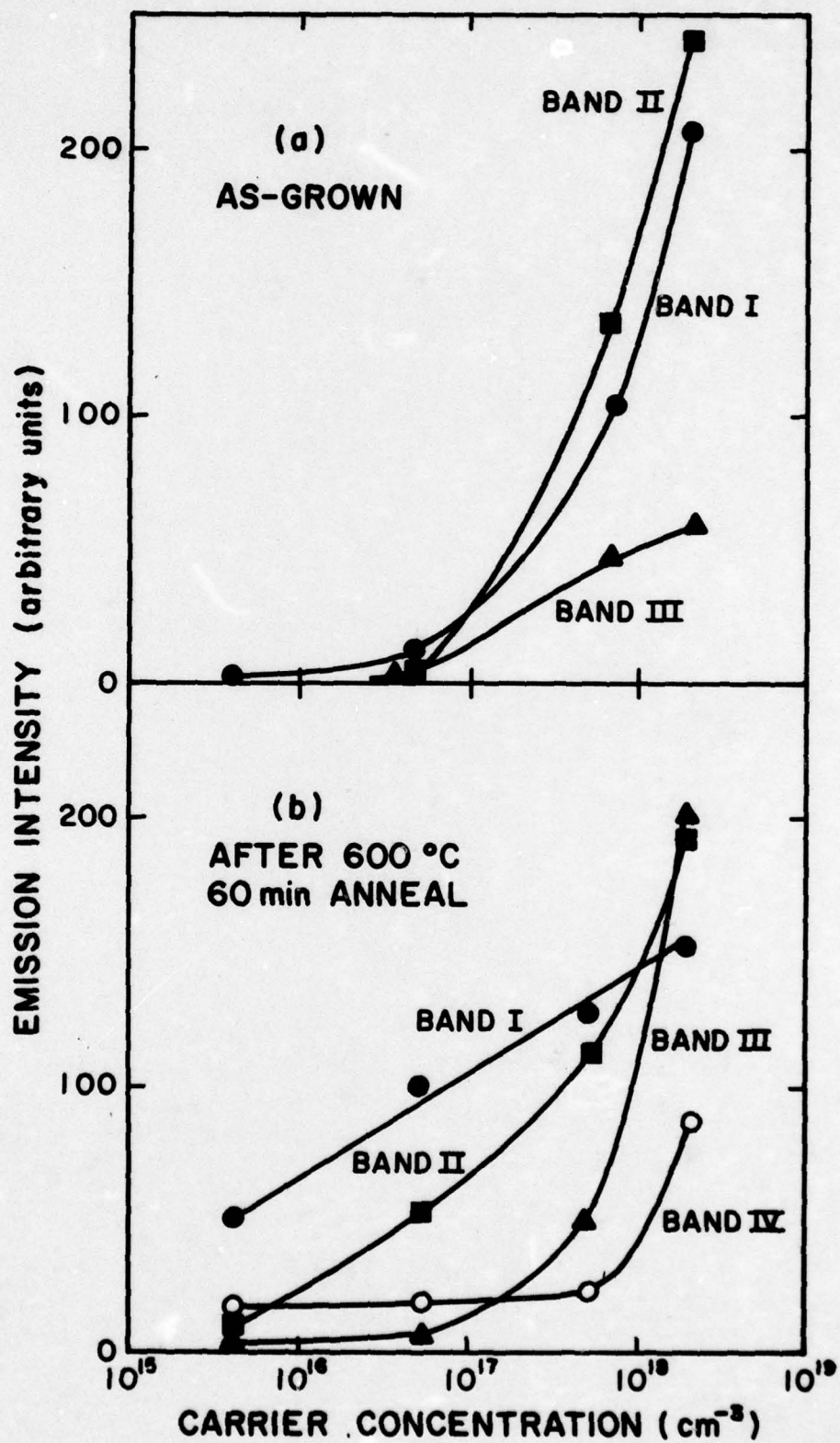


Fig. 2

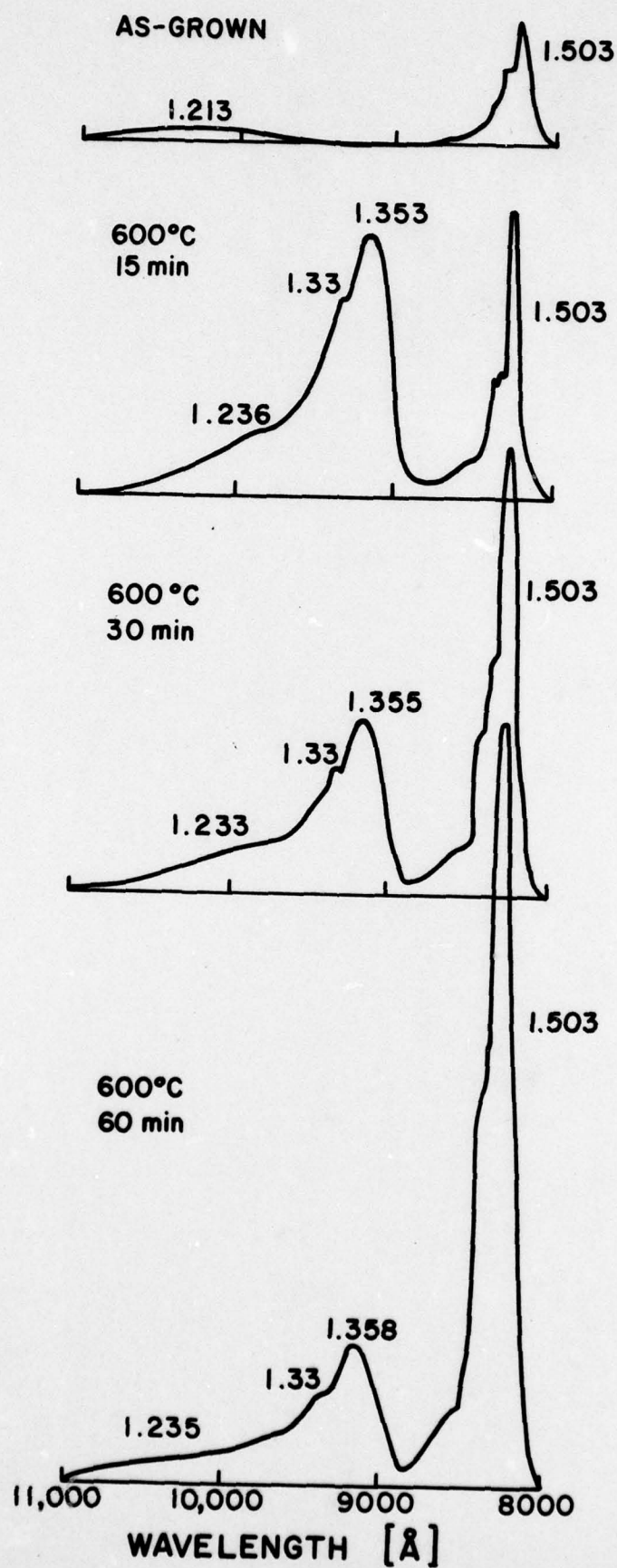


Fig. 3

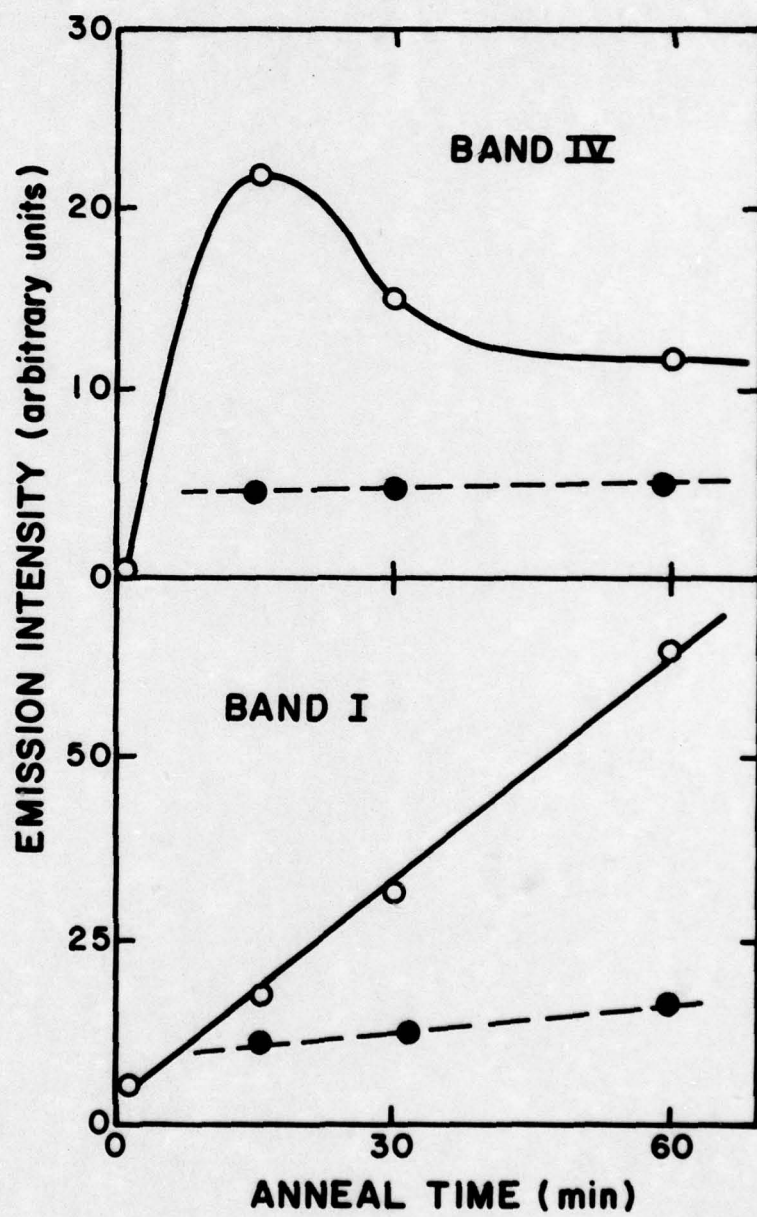


Fig. 4

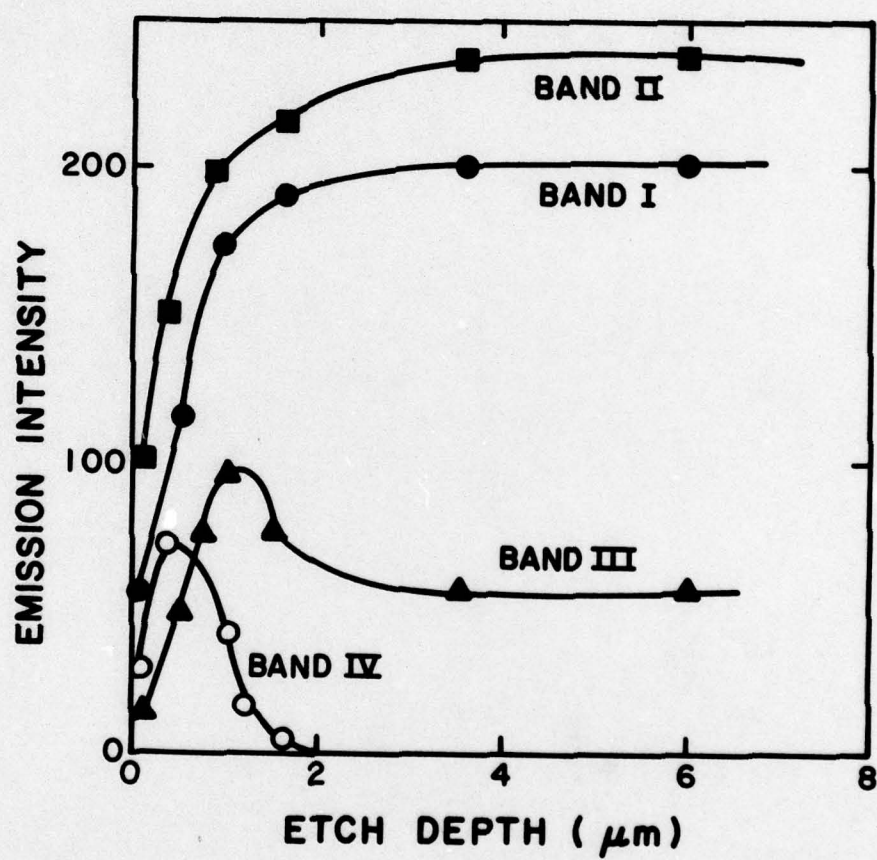


Fig. 5

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